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The use of zeolite as fluxing agent for whitewares

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Abstract

The possibility of natural zeolite utilization as a fluxing agent for sintered ceramic bodies will be determined compared with traditional ceramic flux – feldspar and quartz sand as a grog without fluxing effect. Sintering behaviour as dependence of water absorption of dry pressed test samples made from different fluxes (zeolite, sodium-potassium feldspar) and binder (kaolin) on the firing temperature (1150 – 1300 °C) were analysed. Zeolite is very intensive fluxing agent compared with sodium-potassium feldspar. Zeolite with kaolin creates body (after firing) with lower coefficient of linear thermal expansion. Thanks to higher content of ferric oxides is not suitable for whiteware, because the colour of the sintered body is dark (brown).

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Keywords: Zeolite; whiteware; porosity; fluxing agent

1. Introduction

Zeolite is a natural mineral with exceptional physical properties that follow from its specific crystal structure. The latter consists of a 3D lattice of silicate tetrahedrons $(SiO_4)^{4-}$ mutually connected by oxygen atoms, with part of silicon atoms replaced by aluminium atoms $(AlO_4)^{5-}$. Zeolite has a wide range of applications in agriculture,

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breeding, civil engineering, protection of environment, wastewater purification, and in various industrial sectors. In civil engineering it began to be used as a partial replacement of cement in the production of concrete [1–5].

Low-cost zeolitic rocks were promising substitutes for feldspathic fluxes in ceramic bodies, since their fusibility, modest hardness and high cation exchange capacity (CEC) should improve grinding and sintering. Five large-scale Italian deposits of natural zeolites with different mineralogy were characterised and tested in porcelain stoneware bodies. Their behaviour during processing was appraised and compared with that of zeolite-free bodies. Zeolites increased the slip viscosity during wet grinding, causing a coarser grain size distribution and consequently some drawbacks in both unfired and fired tiles. After overcoming this hindrance by dry grinding of zeolite rocks, the technological behaviour of zeolite-bearing tiles appear to be similar to that of current porcelain stoneware, though with larger firing shrinkage and residual closed porosity. [6]

The aim of the study [7] was to investigate the effect of natural zeolite addition on the sintering kinetics. Clinoptilolite which is a type of natural zeolite was added partially or fully in replacement of quartz at selected electro-porcelain composition. Samples were fired in an electric furnace with a heating rate of 10 °C/min at 1150, 1200 and 1250 °C with a period of 5, 10, 20, 30, 60 and 90 min. The sintered samples were characterized by XRD and SEM. Sintering activation energies were determined according to the bulk density results. It was found that the sintering activation energy decreased with increasing zeolite addition. Replacement of silica with zeolite resulted in reduced activation energy required to start sintering in porcelain samples. Therefore, densification rate could be increased. Depending on the decrease in activation energy, sintering time and temperature were both declined. As a consequence of lower activation energy, it may be possible to produce the porcelain at 1250 °C instead of 1300 or 1350 °C, which would lead to considerable saving in sintering temperature and lower cost by the addition of zeolite. Finally silica could be replaced by zeolite addition in porcelain production and other conclusions to be drawn from this study are summarized as follows:

- Densification increased with the increase in quantity of zeolite addition, sintering time and temperature.
- Bulk densities of the compacts generally increased with the addition of zeolite for all sintering temperature.
- Activation energies of sintered compacts were initially increased with the increase in zeolite addition from zero up to 5% addition then decrease sharply up to 25% zeolite addition.

In the study [8], the effect of natural zeolite addition on the electrical properties of porcelain bodies was investigated. Clinoptilolite, which is a type of natural zeolite, was added partially or fully in replacement of quartz in selected electro-porcelain compositions. Samples were fired in an electric furnace with a heating rate of 10 °C/min at 1200 and 1250 °C with a period of 60 min. The electrical resistance measurements of samples were performed at 50, 200, 400 and 600 °C. It was shown that the resistivity of samples increased at 50 °C temperature after zeolite addition, while it was decreasing after zeolite addition at higher temperatures. At the same time, it was recognized that the resistivity of samples depends on sintering temperature. The activation energy of electrical resistivity of samples was found to be in the range of 0.79–0.87 eV. The present study was designed to determine the effect of electrical resistivity of porcelain bodies with natural zeolite addition.

Low-cost, naturally-occurring mixtures of feldspar and zeolite occurring in epiclastic rocks were promising substitutes for conventional quartz-feldspathic fluxes in ceramic bodies. Three epiclastic outcrops, with a different zeolite-to-feldspar ratio, were characterized (XRPD, fusibility) and tested in porcelain stoneware bodies; their behaviour during processing was appraised and compared with that of a reference. The addition of an epiclastic rock (20 wt.%), replacing rhyolite and aplite fluxes, brought about some significant advantages, mainly represented by better grindability, lower firing temperature with improved mechanical strength and lower porosity. Disadvantages concern increased slip viscosity, worse powder compressibility, resulting in larger firing shrinkage, and a darker colour of the tiles due to relatively high amounts of iron oxide [9].

The aim of the presented article is to compare fired (sintered) bodies based on traditional ceramic fluxing agent – feldspar – and zeolite in the mixture with Czech kaolin.

2. Methodology and materials

Three different raw material mixtures on the basis of washed kaolin (Sedlecky kaolin Czech Republic)) and industrially milled non-plastic materials (grogs and fluxing agents): sodium-potassium feldspar (LB Minerals Czech Republic), quartz sand (Sklopisek Strelec Czech Republic) and natural zeolite (Zeocem Slovakia) were prepared (Table 1) for determination of zeolite influence on the properties of green and fired body.

Table 1. Composition of raw materials mixtures.

Mixture	Kaolin (*wt.-%)*	Quartz (*wt.-%)*	Feldspar (*wt.-%)*	Zeolite (*wt.-%)*
A	25	75	-	-
B	25	25	50	
C	25	-	-	75

The raw material mixtures (Table 1) for the production of the test samples were dry-mixed for 24 hours in the homogenizer. The mixture was then moistened at the pressure moisture 9% and the moistened mixture was pressed through the 1 mm sieve. Granulate was thus prepared and subsequently mixed for 24 hours in the closed vase of the homogenizer to reach a homogenous moisture. Testing samples with a green body size of 100 × 50 × 8 mm were uniaxially pressed at 20 MPa.

Drying in laboratory dryer at a temperature of 105 °C was followed to achieve constant weight. The test samples were fired in the laboratory electric kiln with heating rate 10 °C/min and 30 min soaking time at maximum firing temperature.

Table 2. Typical chemical composition of used raw materials (*%-wt*).

Material	CaO	Al_2O_3	K_2O	Na_2O	SiO_2	Fe_2O_3	MgO	LOI
Kaolin	0.70	36.60	1.20		46.80	0.85	0.50	13.20
Feldspar	0.48	12.37	3.35	2.67	79.76	0.42	0.10	0.80
Zeolite	3.30	12.40	2.80	1.00	68.20	1.40	1.00	

The mineralogical composition of used washed kaolin is 91% of kaolinite, 2% of quartz and about 7% of mica minerals. Mineralogical composition of feldspar: potassium feldspar (microcline) 20.0 %, sodium feldspar (albite) 22.6%, calcium feldspar (anorthite) 2.4% and quartz 55.0%. Mineralogical composition of zeolite: clinoptilolite 84.0%, cristobalite 8.0%, illite 4.0% and plagioclase 4.0%.

The chemical composition of all used materials is clear from table 2. Granulometry of milled non plastic materials (zeolite, feldspar and quartz) was determined according to particle size distribution (Malvern Mastersizer 2000). The equivalent mean spherical diameter of feldspar d (0.5) = 20.8 μm, quartz sand 16.0 μm and zeolite 20.0 μm is suitable for the production of whiteware body.

3. Results and discussion

The dilatometric heating and cooling curves dL/L0 of two different samples according to fluxing agent utilization (zeolite vs. feldspar) are shown in Fig. 1. During the firing, there is evident (Fig. 1) that zeolite (mixture C) is more intensive fluxing agent compared to feldspar for the creation of sintered body with low porosity. High firing shrinkage is typical for the sintering – the raw materials mixture C with zeolite content starts intensive shrinking from temperature of about 900 °C. Compared mixture B with traditional ceramic fluxing agent – feldspar – beginning the sintering process only from a temperature of about 1100 °C.

The quartz transformation at 573 °C (change of the fired body volume) is visible on cooling part of dilatometric curve of the mixture B thanks to high portion of quartz in the mixture B (Table 1). This phenomenon is not presented on the cooling curve of the sintered body C based on zeolite – the raw materials mixture not contains

quartz, which is advantageous for lower relative expansion (coefficient of linear thermal expansion – Fig. 3) of sintered body C.

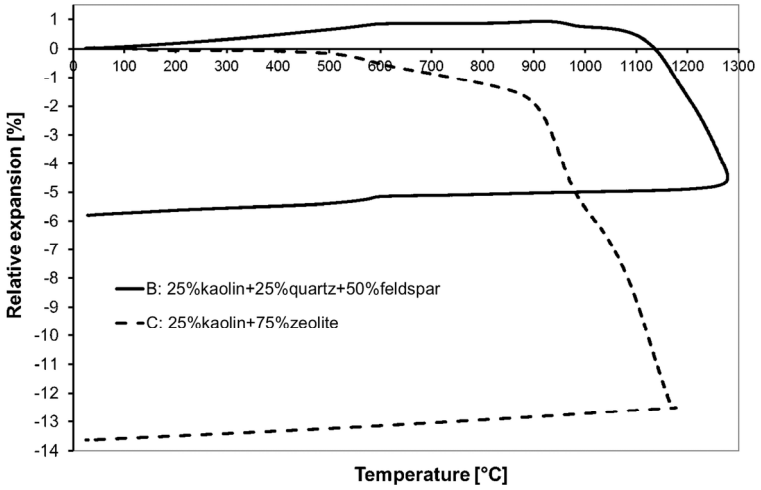

Fig. 1. Dilatometric analysis during the firing (5 °C/min without soaking time).

Sintering activity of dry tested samples based on different kinds of fluxing agents according to dependence of water absorption on the firing temperature was determined. The most intensive sintering of the body is visible (Fig. 2) when zeolite was used – the test samples show the lowest water absorption. The most exact parameter for sintering process description is sintering temperature, which is defined as temperature when the fired body has water absorption E = 2 % (Fig. 2). Sintering temperature of tested samples based on zeolite is 1180 °C which is about 100 °C lower than for the sample based on standard flux feldspar (mixture B).

From the picture (Fig. 3) there is evident different coefficient of linear thermal expansion α (in the temperature range of 30 – 500 °C) of both compared sintered bodies (B vs. C):

$\alpha_{30\text{-}500°C}$ (B) = 70×10^{-7} K^{-1}

$\alpha_{30\text{-}500°C}$ (C) = 48×10^{-7} K^{-1}

The sintered body based on zeolite shows the lower coefficient of thermal expansion α compared with feldspar sample due to the formation of anorthite in the sample C (Fig. 4 and Table 3) and absence of quartz. Important technical property of anorthite is its low coefficient of linear thermal expansion of 48.2×10^{-6} K^{-1} [10] (mullite 60×10^{-7} K^{-1} [11]). The mineralogical composition of both bodies after firing in both cases is characterized by the existence of mullite and glass phase. The sintered body (fired at 1200 °C – mixture C or 1300 °C – mixture B respectively) based on feldspar and quartz (mixture B) also contains quartz, the body made from zeolite contains anorthite and cristobalite (Fig. 4 and Table 3).

There is evident (Fig. 5) that sintered body based on zeolite as a fluxing agent not creates white body which is typical for sintered body of the mixture B based on sodium – potassium feldspar. This situation corresponds to chemical composition of natural zeolite with higher content of Fe_2O_3 (Table 2).

Table 3. Mineralogical composition of sintered bodies.

Sintered body	Mineralogical composition
B (1300 °C)	Quartz, mullite
C (1200 °C)	Mullite, cristobalite, anorthite

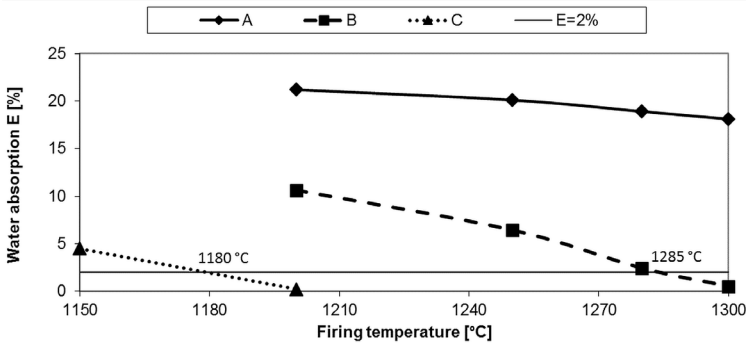

Fig. 2. Water absorption of tested bodies A, B, C depending on firing temperature. Determination of sintering temperature.

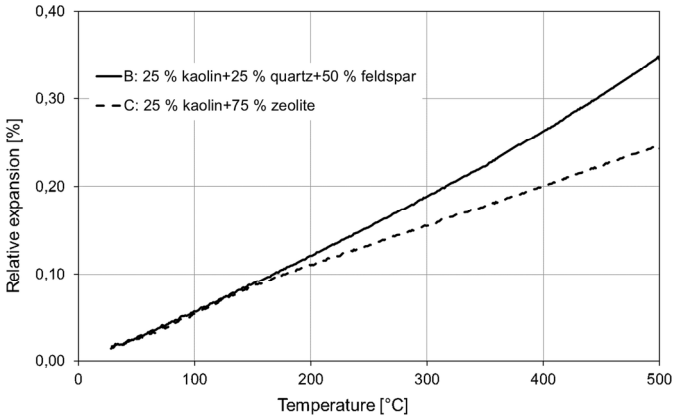

Fig. 3. Relative expansion of sintered bodies.

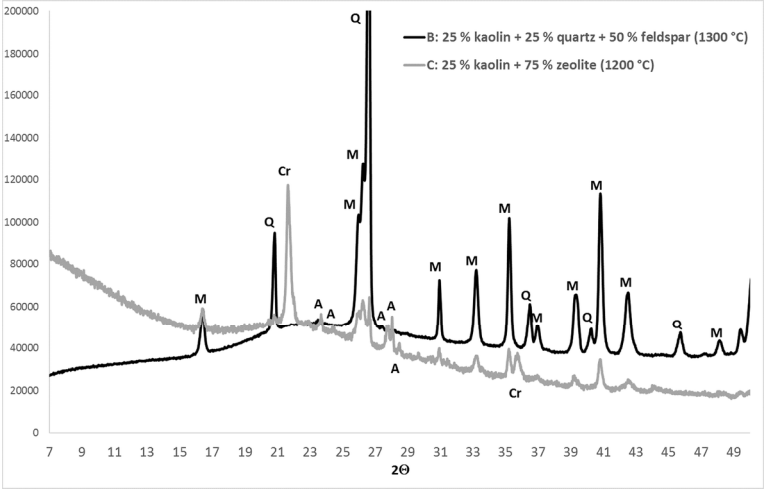

Fig. 4. X-ray diffraction analyzes of tested sintered bodies: mineralogical composition: M-mullite, Q-quartz, A-anorthite, Cr-cristobalite.

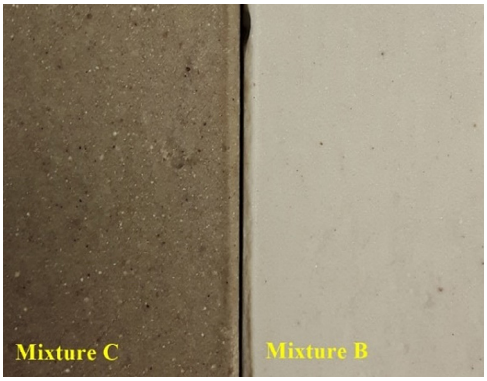

Fig. 5. Color of sintered bodies with water absorption below 2%.

4. Conclusion

Natural zeolite is very intensive fluxing agent for ceramic technology. Using zeolite we can reduces the sintering temperature of the body of about 100 °C, compared with traditional ceramic fluxing agent – sodium-potassium feldspar. The sintered body (with water absorption below 2 %) based on zeolite has lower coefficient of linear thermal expansion. Presence of zeolite in raw materials mixture significantly changes mineralogical composition of fired whiteware body – mullite, anorthite and cristobalite are the main mineralogical phases instead of mullite and quartz which are typical for a standard whiteware bodies made from raw material mixtures based on kaolin, quartz and feldspar. The limiting factor for the use of natural zeolite as a flux for whiteware is its coloring effect.

Acknowledgements

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